

SOME SMALL-ANGLE X-RAY SCATTERING TECHNIQUES FOR
STUDYING THE SUBMICROSCOPIC STRUCTURE OF COALS AND COAL-DERIVED LIQUIDS

Paul W. Schmidt, Chul Y. Kwak, and Mohanan Kalliat

Physics Department, University of Missouri, Columbia, MO 65211

Small-angle x-ray scattering is often useful for investigating submicroscopic structures--that is, structures with dimensions between about 20 and 2000 Å (1). This technique has been employed in several studies of the porosity and other submicroscopic structure of coals (2--7).

In this review, we will summarize the results we obtained in Reference (7), and we will discuss briefly some of our more recent scattering studies of coal porosity (8). We also will illustrate how scattering techniques can provide useful information about the properties of coal-derived liquids aged under oxygen for periods up to 8 weeks (9).

First, however, we will review some of the methods and techniques which we employed in our interpretation of the small-angle x-ray scattering data from coals. Figure 1 is a schematic drawing of a small-angle x-ray scattering system. X-rays from the tube T are formed into a beam by slits and fall on the sample S. A small fraction of the x-rays striking the sample are re-emitted, without change of wavelength, in directions different from that of the incoming beam. The intensity of these re-emitted x-rays, which are called the scattered rays, and their dependence on the direction in which they are emitted depend on the structure of the sample. In a scattering experiment, the intensity of the x-rays scattered in different directions is measured, and from an analysis of these data, an attempt is made to obtain information about the structure of the sample producing the scattering. Figure 1 shows a ray scattered at an angle θ with respect to the incoming beam. The scattered radiation is recorded by the detector C.

While no universal prescription can be given for analyzing the scattering pattern from an arbitrary sample, we will review some general principles useful for interpretation of scattering measurements. For a sample which has a structure characterized by a dimension a , most information obtainable from scattering measurements will be found at scattering angles θ in an interval for which

$$0.1 < ha < 10, \quad (1)$$

where $h = (4\pi/\lambda) \sin(\theta/2)$; and λ is the x-ray wavelength. For angles no greater than about 7 degrees, $\sin \theta/2$ can be approximated by $\theta/2$, and so for small scattering angles, h can be considered proportional to θ . According to (1), for a structure with dimension a , the scattering is determined by the product ha , so that there is an inverse relationship between the size of the structure and the h values at which the scattered intensity from this structure is appreciable. Since the x-ray wavelengths are normally of the order of 1 or 2 Å and thus are of the same magnitude as the interatomic spacing in solids and liquids, Inequality (1) states that the x-ray scattering from structures with dimensions between about 20 and 2000 Å will be observed at scattering angles no greater than a few degrees. Small-angle x-ray scattering thus can be used to study these submicroscopic structures.

X-rays are scattered by electrons, and the small-angle scattering will be appreciable when the sample contains regions in which fluctuations or variations in electron density extend over distances of 20 to 2000 Å. At small angles, the scattering process is unable to resolve structures smaller than about 10 Å, and so in the analysis of the scattering data, the atomic-scale structure can be

neglected. For many scattering studies, it is therefore convenient to consider the sample to be composed of two phases, with constant but different electron densities.

If this two-phase approximation holds and the two phases always are separated by a sharp, discontinuous boundary, when the minimum characteristic dimension a_m of the structure satisfies the condition $ha_m > 3.5$, the scattered intensity $I(h)$ can be approximated by (7)

$$I(h) = \frac{2\pi\rho^2(S/M)}{h^4} \frac{M}{A} I_e A, \quad (2)$$

where ρ is the difference of the electron densities of the two phases, I_e is the intensity scattered by a single electron; S is the total surface area separating the two phases in the sample; M is the mass of the sample; and A is the cross-sectional area of the sample perpendicular to the incident beam. In the outer part of the small-angle scattering curve--that is, when $ha_m > 3.5$, the scattered intensity is proportional to h^{-4} and thus to the inverse fourth power of the scattering angle. Moreover, when $I(h)$ has this angular dependence, the magnitude of the scattered intensity is proportional to the specific surface S/M , which is the surface area per unit sample mass separating the two phases.

As we explain in Reference (7), the quantities $I_e A$ and M/A can be evaluated from the x-ray data, and so Equation (2) can be employed to calculate the specific surface S/M from the scattering data for samples with submicroscopic porosity.

We have made use of this technique to determine the specific surfaces of a number of PSOC coals. As our x-ray studies showed (7) that the almost all of the small-angle x-ray scattering was due to pores and that the scattering from the mineral matter in the coal was almost negligible, we have interpreted the small-angle x-ray scattering from coals as being due to submicroscopic pores, which are filled with air and for scattering purposes thus are essentially empty.

Our scattering studies show (7) that the rank of the coal is the main factor which determines the form of the angular dependence of the scattered intensity. The scattering curves for the coals which we studied can be grouped in four classes, as Figure 2 illustrates. Since both axes of Figure 2 are logarithmic, the curves in Figure 2 are straight lines with slopes -4 when Equation (2) describes the scattering. An angular dependence of this form is obtained for all types of coals at the smallest angles at which data could be recorded--that is, for scattering angles smaller than about 0.005 radian. For Pennsylvania Buck Mountain anthracite coal (PSOC 81, triangles), this inverse-fourth power continues to scattering angles as large as about 0.015 radian, and then the intensity decreases less rapidly with increasing scattering angle. Of all coals shown in Fig. 2, the scattering in the outer part of the plot is most intense for the anthracites. We interpret (8) this result as being due to the presence of a relatively large number of micropores, with average dimensions smaller than about 30 Å. As we have obtained similar curves for other anthracites, we have concluded that in these high-rank coals, there is a large fraction of micropores and an appreciable number of macropores, which have dimensions of 1000 Å or more. In a low-rank coal like Washington Queen #4 (PSOC 95, circles), there also are macropores, but since in the outer part of Fig 1 the intensity is lower than for the anthracite, we conclude that the anthracites have a larger fraction of micropores. Lignites gave scattering curves similar to the curve for PSOC 95. In the scattering curves for low volatile bituminous coals like Pennsylvania E. Kittanning coal (PSOC 127, plus signs), there is a maximum near 0.080 radians. This maximum has been ascribed (10) to interactions between the fundamental scattering units in these coals, which are planar aggregates of aromatic rings. In the fourth type of curve in Fig. 2, which we obtained for Illinois No. 6 coal (PSOC 22, squares) and for many other but not all low and medium-rank bituminous

coals, there is a shoulder on the scattering curve at intermediate scattering angles. On both sides of the shoulder or inflection, the intensity is proportional to the inverse fourth power of θ . (The shoulder on the curve in Fig. 3 occurs at such small angles that in this curve the inner region where the intensity is proportional to the inverse fourth power of θ is barely visible.) As we explain in Reference 7, we consider this shoulder to be the result of the fact that in these coals, there is a relatively high fraction of transitional pores, with average dimensions of the order of 50 to 200 Å. We calculated a specific surface from each part of the scattering curve which was proportional to the inverse fourth power of θ . These two surfaces are the specific surfaces of the macropores and the transitional pores. We have found that the presence of an inflection in the scattering curve is an indication that the coal has a relatively large number of transitional pores.

At the time we wrote the manuscript for Reference (7), we were unable to relate this high fraction of transitional pores to any other property of the coals. We have now found (8) that there are inflections only in coals with fixed carbon contents in the interval from about 72% through 83% per cent (dry, mineral-matter free). These results are summarized in Figure 3, which is a preliminary plot of the sum of the specific surfaces of the macropores and transitional pores as a function of carbon content.

The ability to distinguish between the specific surfaces associated with the macropores and the transitional pores is, we feel, a unique property of small-angle x-ray scattering.

By making some reasonable assumptions, we have also been able to estimate the specific surfaces and dimensions of the micropores in many coals (8).

The value of the specific surface obtained in studies of porous materials often depends on the techniques used for the measurement. For example, Gan, Nandi, and Walker (11), in their adsorption studies of a number of PSOC coals, obtained much larger specific surfaces by carbon dioxide adsorption at room temperature than by low-temperature adsorption of nitrogen. As we mentioned in Reference (7), the difference may be the result of the fact that carbon dioxide at room temperature can penetrate smaller pores than can be entered by nitrogen molecules at low temperature (12). As can be seen by comparison of the magnitudes of the specific surfaces in Figure 3 with the nitrogen specific surfaces in Figure 1 of Reference (11), the x-ray specific surfaces are much nearer to those measured by low temperature nitrogen adsorption than by room temperature carbon dioxide adsorption. As the micropores are too small to satisfy the conditions necessary to give a scattered intensity proportional to the inverse fourth power of the scattering angle, the "x-ray specific surface" includes only contributions from the macropores and transitional pores and does not take account of the specific surface of the micropores.

With reasonable assumptions, the dimensions and the specific surface of the micropores in anthracites and, at times, other coals can be estimated from the small-angle scattering data.

We have recently completed a small-angle x-ray scattering study of some coal-derived liquids prepared from West Virginia Ireland Mine coal in the U. S. Department of Energy Pittsburgh Energy Technology Center 400 lb/day Bruceton Liquefaction Unit and aged under oxygen for different lengths of time (9). To analyze the scattering data, we used the radius of gyration approximation, according to which, for independently-scattering, randomly-oriented particles (Ref. 1, pp. 24-28),

$$I(h) = I(0) e^{-(h^2 R^2/3)}, \quad (3)$$

where $I(0)$ is the zero-angle scattered intensity, and R , the radius of gyration, is a characteristic dimension of the particle. According to Equation (3), which approximates the scattering when hR is not large with respect to 1, a plot of the logarithm of the scattered intensity as a function of the square of the scattering angle should be a straight line, from the slope of which the radius of gyration can be calculated. In Fig. 4, the radius of gyration plots, which are at least approximately linear, show that the radii of gyration of the coal-derived liquids, and thus the average size of the particles, at first grows slowly, but after the sample is aged for more than 4 weeks, there is a sharp rise in the radius of gyration. This increase in the radius of gyration is accompanied by a large increase in the viscosity. The scattering data thus relate the rise of the viscosity to the presence of relatively large, agglomerated colloidal particles in the coal-derived liquids.

By use of helium density and chemical composition measurements of the coal-derived liquids, we were able to show that in the early stages of aging--that is, before appreciable agglomeration took place, the number of colloidal particles remained essentially constant, and that the main effect of aging was to cause the colloidal particles already present to grow larger, rather than to produce new particles. We also have been able to make a rough estimate of the fractions of the volume occupied by the small and large colloidal particles.

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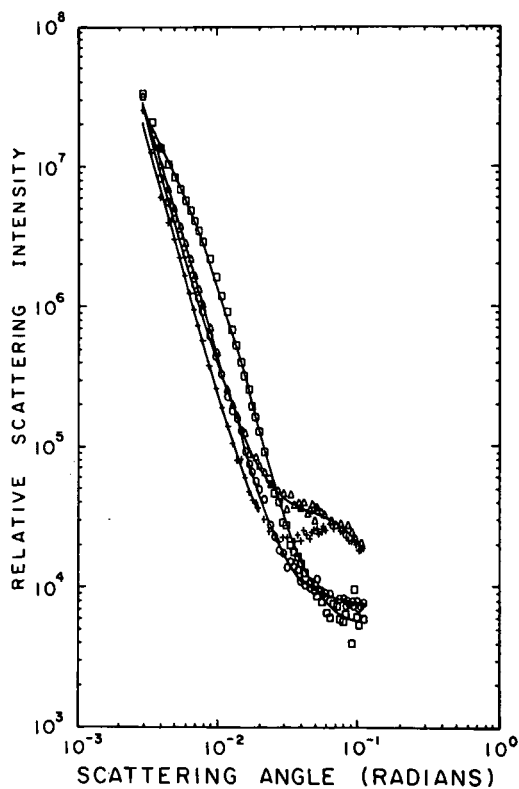
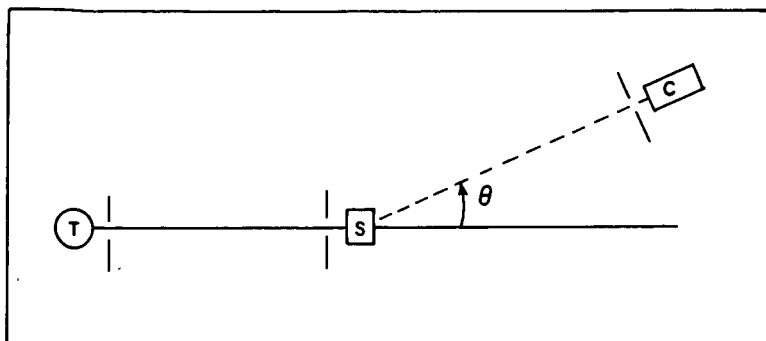


Fig. 1. (above) Schematic diagram of a small-angle x-ray scattering system. (Reproduced from Reference 7 by permission of the American Chemical Society.)

Figure 2. (left) Typical scattering curves for the coal samples. Curves 1--4 show the data for PSOC coals 95 (circles), 127 (plus signs), 81 (triangles) and 22 (squares). (This plot is reproduced from Reference 7 by permission of the American Chemical Society.)

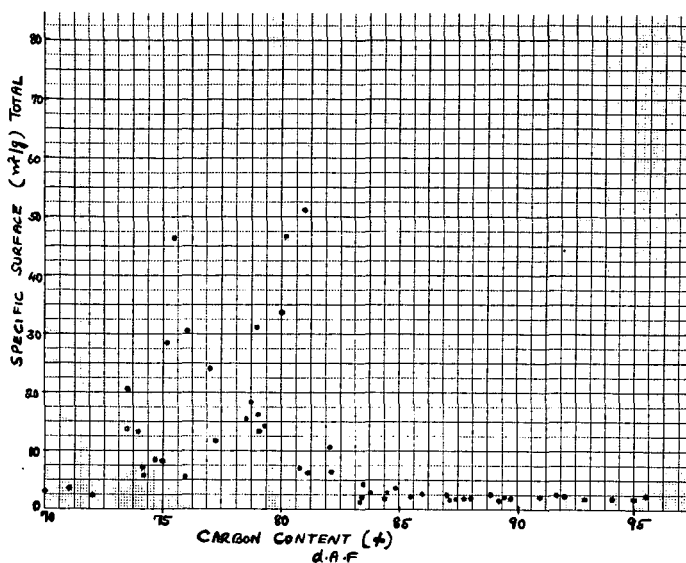


Figure 3. The combined x-ray specific surfaces of the macropores and transitional pores for coals of different carbon content (dry, ash-free).

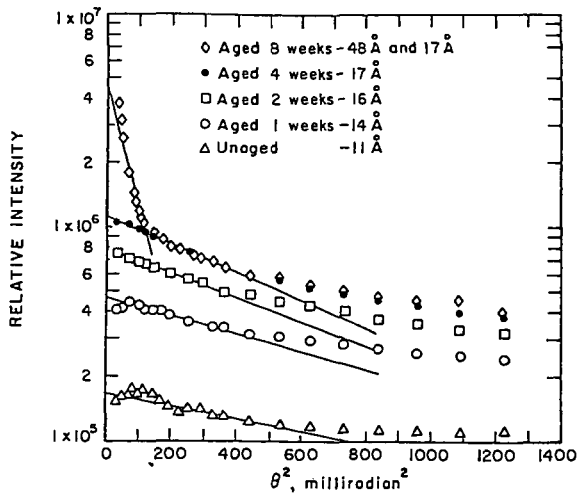


Figure 4. Radius of gyration plots for the coal-derived liquids.